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Synthesis and Properties of New Phosphorus-Functionalized Bithiophene Materials

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Summary: The synthesis and reactivity of the novel dithieno[3,2-*b*:2',3'-*d*]-phosphole system and its potential use in polymeric sensory materials was investigated. Due to the nucleophilic nature of the phosphorus atom, these materials were found to be easily tunable. Classical reactions at the phosphorus center were performed to modify the electronic structure of the system and the corresponding changes were detected by UV/Vis and fluorescence spectroscopy. Depending on the oxidation state of the central phosphorus atom or its substitution pattern, the dithieno[3,2-*b*:2',3'-*d*]-phospholes show varying wavelengths for absorption and emission allowing to distinguish between different compounds by means of optical spectroscopy.

Keywords: fluorescence; phospholes; polymeric sensors; thiophenes

Introduction

The incorporation of thiophene moieties into oligomeric or macromolecular systems has recently become a topic of significant interest due to their highly intriguing properties.[1] A variety of such conjugated polymers exhibit a striking ability; ultrafast energy transfers that leads to a metal-like conductivity. The resulting materials therefore show great potential for applications in electronic devices such as organic light-emitting diodes (OLEDs), photovoltaic cells, flat panel displays or polymeric sensors.[2] However, the introduction of the corresponding electronic properties is often connected with synthetic difficulties that would significantly increase the production costs of the resulting devices. This could keep them from industrial applications. Since the optoelectronic properties of, for example, the classic poly(phenylenevinylidene) (PPV) system is limited to certain emissions, doping is very important in order to increase the potential for applications.[3] A great deal of attention has therefore been focused on the tuning of the

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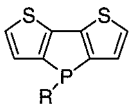
optoelectronic structure of the polymeric systems in order to modify their electronic nature (i.e. band gap) in such a way that it suits the targeted application.[4]

As part of our research on the development of processable, electronically active, macromolecular inorganic materials we have focussed on the novel dithieno[3,2-*b*:2',3'-*d*]phosphole moiety. This system should allow selective tuning of the electronic properties of the materials by functionalization of the central phosphorus atom. Like almost no other element, phosphorus is particularly suited to act as a bridging element in the dithieno system due to its nucleophilic nature. Its ability to react with oxidizing agents such as oxygen or sulfur, its Lewis basicity which allows reactions with Lewis acids such as BH_3 in addition to the potential for coordination to transition metals offers a unique variety of synthetically facile possibilities to modify the electronic properties of the dithienophosphole materials. In this paper we report on our initial studies in this area and describe model compounds for prospective polymeric materials, their chemical modification, and their electronic properties.

Results and Discussion

We have targeted the investigation of the novel dithieno[3,2-*b*:2',3'-*d*]phosphole system (**1**) since it combines two favorable properties; excellent π-conjugation between the two thiophene subunits and 'guided' electronic doping through the phosphorus center. It should be mentioned in this context that the number of dithieno systems is very limited. The only known examples involve carbon, nitrogen, silicon and sulfur as bridging elements (**2**).[5] The use of phosphorus has only been reported in compound **3**[6]; σ^3-λ^3 phosphorus-based systems (**1**) on the other hand have been completely unknown to date.



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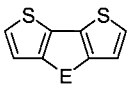

E= CR_2, NR, SiR_2, S, SO, SO_2

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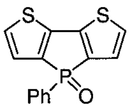

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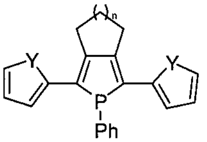
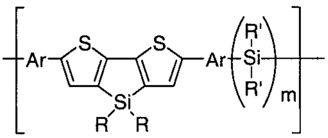
The advantageous electronic features of the phosphorus center in phospholes have recently been pointed out by Réau and coworkers who incorporated the phosphole moiety into extended thiophene containing π-conjugated systems.[7] In the context of their work they were able to show that the reduced aromatic character (compared to furan, pyrrole or thiophene) leads to intriguing electronic properties. Due to the pyramidalization of the phosphorus center, an efficient orbital interaction with the conjugated π-system is reduced. As a result, the lone pair at the phosphorus atom only functions as a dopant for the phosphole π-system. The strength of this doping effect depends on the geometry of the phosphorus center. The effect can easily be switched from *n*-type (electron donor) to *p*-type (electron acceptor) by formal oxidation from P(III) to P(V). Réau's phenyl, pyridine or thiophene-substituted materials **4** have proven to be useful synthons for the synthesis of polymeric π-conjugated systems whose electronic properties can be easily tuned over a wide range by performing simple chemical modifications.[7] However, in their case the rings are connected through solely a single bond, which allows for twisting between the central ring and the adjacent units that can reduce the π-conjugation.



n = 3,4; Y = CH=CH; CH=N, S

4



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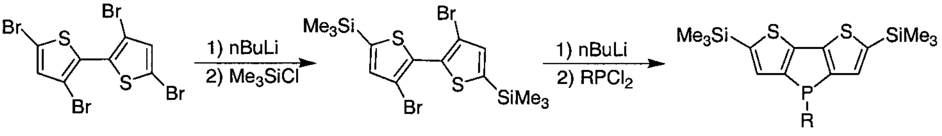
The incorporation of the phosphole moiety into a rigidified tricyclic dithieno system on the other hand should lead to a significantly higher degree of π-conjugation since the annulation of aromatic rings has been found to be a powerful approach to tune the band gap of conjugated polymers.[8] This is further supported by a recent theoretical investigation which has shown that thiophene-based, fused tricyclic polymers show a much more favorable band gap than the related polythiophenes.[9] In this context, Ohshita and coworkers have shown that the incorporation of silicon into the rigid dithieno system (**2**, R = SiR_2) reduces the HOMO-LUMO gap significantly due to the extended conjugated π-system and allows for application as hole transport materials (**5**) in electro luminescent (EL) devices.[10] Taking into account the result of the above-mentioned studies it seemed necessary for us to incorporate an electron-acceptor into the system as well to obtain the targeted HOMO-LUMO separation. We decided on silyl groups, since they can be introduced easily and exhibit suitable acceptor properties by 'negative hyperconjugation'.[11]

Applying Ohshita's strategy for dithienosiloles[10] to our system, we were able to synthesize the novel dithieno[3,2-*b*:2',3'-*d*]phospholes with the desired silyl functionality. Starting from the tetrabromo-dithiophene **6**, the trimethylsilyl groups were introduced first by reaction with *n*-butyllithium followed by addition of Me_3SiCl. Subsequent lithiation of **7** with *n*-butyllithium followed by quenching with $RPCl_2$ (R= Ph, 4-*t*Bu-C_6H_4, *t*Bu) cleanly afforded the first dithieno[3,2-*b*:2',3'-*d*]phospholes **8**:

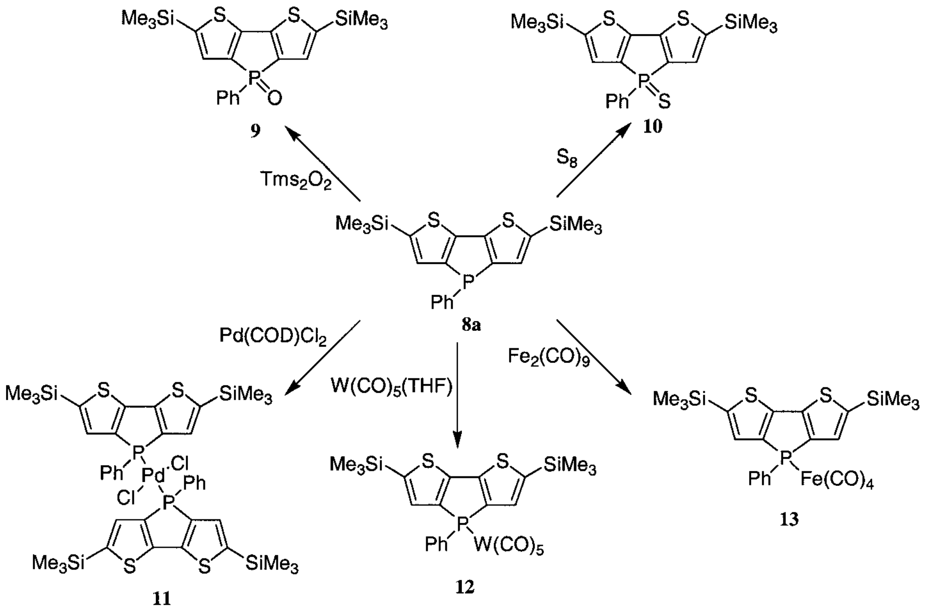


6 **7** **8**

Compounds **8** exhibit ^{31}P NMR shifts (**8a**: R = Ph; δ = -25.0 ppm; **8b**: R = 4-*t*Bu-C_6H_4; δ = -25.9 ppm; **8c**: R = *t*Bu; δ = 2.8 ppm) which are significantly high field-shifted from related phospholes, e.g. those reported by Réau et al. ($\delta^{31}P$ = 11 – 45 ppm)[7]. This indicates a higher electron density at the phosphorus atom likely due to the increased degree of π-conjugation in **8**. To our satisfaction, compounds **8** showed a strong blue fluorescence, supporting the desired optical properties (*vide infra*).

In order to alter the electronic structure of the dithieno[3,2-*b*:2',3'-*d*]phosphole system, we performed classical reactions that utilized the nucleophilic nature of the σ^3-λ^3 phosphorus center. Reaction of **8a** with bis(trimethylsilyl)peroxide or sulfur resulted in the clean formation of the phosphine oxide **9** and the sulfide **10**, respectively. The oxidized species **9** exhibits a ^{31}P NMR shift at δ = 17.2 ppm which shows the expected low field shift for phosphine oxides in comparison to **8**. However, **9** is still high field-shifted from related systems ($\delta\ ^{31}P \approx 45$ ppm)[7]. The same is true for the sulfurized species **10** ($\delta\ ^{31}P$ = 23.6 ppm; c.f. $\delta\ ^{31}P \approx 53$ ppm [7]).

In order to prove its ability to act as a ligand for transition metals, dithienophosphole **8a** was reacted with $Pd(COD)Cl_2$, $W(CO)_5(THF)$ and $Fe_2(CO)_9$. All three reactions were performed at room temperature and afforded the corresponding complexes **11**-**13** in good yields. In contrast to the inorganic compounds **8**-**10**, whose solutions were almost colorless, the solutions of these organometallic complexes were significantly colored (**11**: dark orange, **12**: red, **13**: yellow) indicating electronic interactions of the ligands with the metal centers. The ^{31}P NMR data of the metal complexes again showed the expected low field shift but were, as before, relatively high field-shifted in comparison to related known complexes (**11**: δ ^{31}P = 1.5 ppm[12]; **12**: δ ^{31}P = -7.9 ppm,[7,13] ^{1}J(P,W)= 228 Hz; **13**: δ ^{31}P = 49.9 ppm[14]).



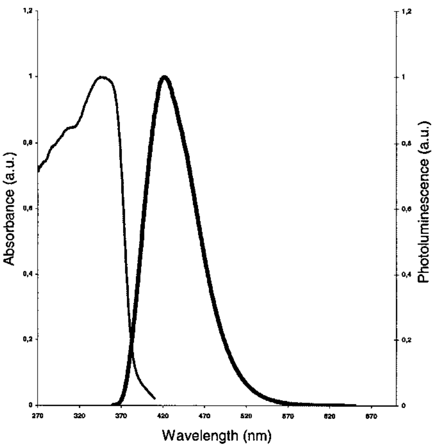
Optical Properties

As previously mentioned, the dithienophospholes **8** exhibit a strong blue fluorescence. This feature opens up a great potential for applications since the detection of fluorescence is rapidly becoming a method of choice in materials science and optoelectronics in addition to medical or environmental studies.[15] Due to its highly sensitive, selective and safe nature it allows for example the observation of living processes or electronic transitions in progress. In materials the presence of luminescence can reflect the delocalization and polarization of the electronic structure.[16] Therefore, changing this electronic structure should have an effect on the luminescence properties. This can be easily detected for the case of fluorescence phenomena, and would allow for the application of dithienophospholes as sensory materials once a library for different derivatives is created.

For this reason we investigated the UV/Vis and fluorescence properties of **8a**, **9**, **10** and **11**, four representative systems involving either a σ^3-λ^3 phosphorus center, one of two different σ^4-λ^5 phosphorus centers, or a transition metal-substituted phosphorus center. The UV/Vis spectra in CH_2Cl_2 show different absorptions for the four compounds, which are partially dependant on the oxidation state of the phosphorus center. As a result **8a** and **11** show similar absorptions at ca. 344 nm with an additional shoulder at 425 nm for **11** presumably indicating the optical features of the transition metal center. Likewise, the oxidized σ^4-λ^5 compounds **9** and **10** show similar absorptions to each other at ca. 373 nm. These initial results indicate that the oxidation state of the phosphorus atom in related systems could ultimately be detected by UV/Vis analysis.

More detailed information was obtained from the fluorescence spectroscopic data. The fluorescence spectra for **8a**, **9**, **10** and **11** (Figures 1–4) in CH_2Cl_2 not only revealed different *wavelengths* for absorption and emission but correspondingly different *intensities* for the fluorescence which may prove to be helpful for the detection of chemically closely related compounds.

As expected, the four compounds show different absorption/emission wavelengths reflecting the electronic nature of the different systems. The values for the σ^3-λ^3 phosphorus-containing system **8a** appear at lower wavelengths [x (excitation) = 344 nm; m (emission) = 422 nm] which is coherent with the electron-donating nature of the P-lone pair. Oxidation of the phosphorus atom causes switching from electron donor to electron acceptor and hence to a energetically more favorable system (**9**/**10**: x = 374 nm, m = 460 nm). The values for the palladium complex **11** (x = 384 nm, m = 470 nm) can be explained by electronic interactions between the dithienophosphole ligand and the transition metal center.



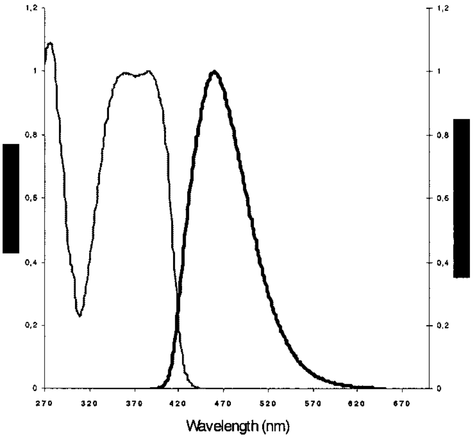
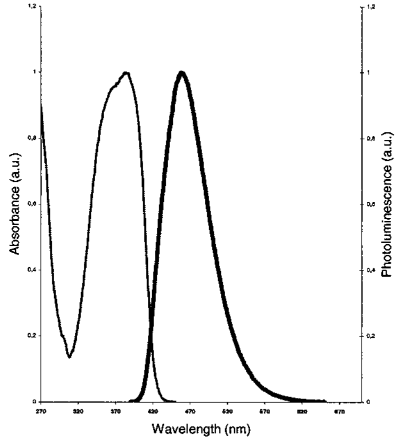


Figure 1 (left): Absorption (left) and photoluminescence (right) spectrum of a 5x10^{-5} M solution of **8a** in CH_2Cl_2.

Figure 2 (right): Absorption (left) and photoluminescence (right) spectrum of a 1x10^{-4} M solution of **9** in CH_2Cl_2.



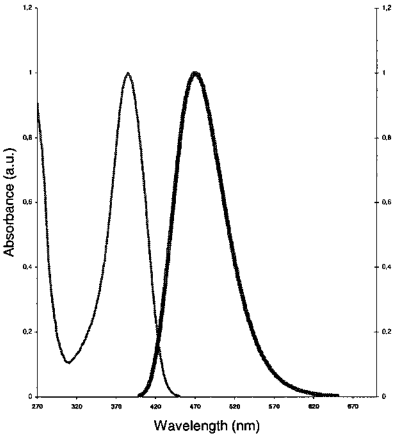


Figure 3 (left): Absorption (left) and photoluminescence (right) spectrum of a 1x10^{-4} M solution of **10** in CH_2Cl_2.

Figure 4 (right): Absorption (left) and photoluminescence (right) spectrum of a 3x10^{-5} M solution of **11** in CH_2Cl_2.

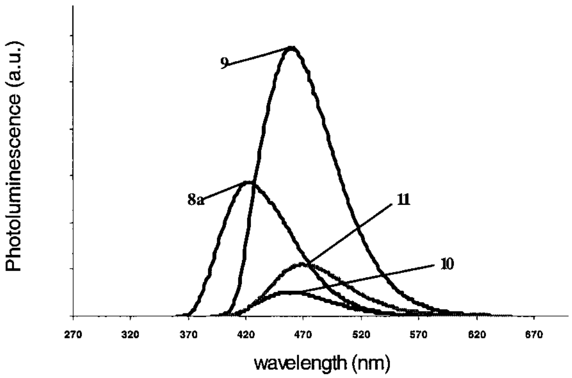


Figure 5: Photoluminescence spectra of **8a** (c = 5x10^{-5}M), **9** (c = 1x10^{-4}M), **10** (c = 1x10^{-4}M) and **11** (c = 3x10^{-5}M) - relative intensities.

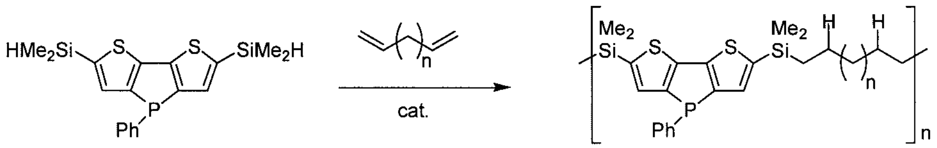
Due to the similar nature of oxygen and sulfur, compounds **9** and **10** exhibit similar absorption/emission wavelengths. However, it is possible to distinguish between them, since they show significantly different fluorescence intensities (ratio approx. 5:1 for **9**:**10**) suggesting that the fluorescence phenomenon is quenched significantly by the sulfur substituent. The relative intensities (with concentrations) of **8a** – **12** are shown in Figure 5. Taking the intensity for compound **10** as a standard, the intensity for **11** is almost three times higher whereas the intensity for compounds **8a** and **9** shows the strongest fluorescence that amounts to approximately five times the intensity of **10**.

Conclusion

Our initial investigations on the novel dithieno[3,2-*b*:2',3'-*d*]-phosphole system resulted in the synthesis of a number of differently-substituted phosphole centers whose electronic properties were found to be easily tunable via simple chemical modifications at the phosphorus center. An additional tuning of this system should be possible by introduction of different exocyclic substituents at phosphorus atom, using the same synthetic strategy. The novel $\sigma^3\lambda^3$ phosphorus-based dithienophospholes, their $\sigma^4\lambda^5$ derivatives, and the corresponding organometallic complexes showed an intriguing feature - fluorescence - that opened up the detection of different species by means of optical spectroscopy. Depending on the electronic nature of the phosphorus center different wavelengths for absorption/emission and intensities were found. These results support the potential use of the novel dithieno[3,2-*b*:2',3'-*d*]phospholes as sensory materials. In the case of the strongly fluorescent compounds **8** and **9** another application as blue emitting materials seems to be possible as well.

Work in Progress

In order to achieve better processability for the use of dithienophospholes as sensory materials it would be advantageous to incorporate this moiety into macromolecular systems. Since recent investigations have shown the presence of silyl substituents is necessary for strong fluorescence[17], the incorporation of silyl centers into the polymeric system would also be highly desirable. A possible route to this goal could be realized by the following method:



8d **14**

The possibility to perform hydrosilylation reactions with the SiH-functionalized compound **8d** is currently under investigation and will be presented elsewhere.

Acknowledgments

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